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A stern-gerlach, time-of-flight search for $^6S_{5/2}$ state of nitrogen*

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Abstract : We have used the method of Stern-Gerlach, time-of-flight in order to search, identify and measure the magnetic properties of the reported $^6S_{5/2}$ metastable state of atomic nitrogen. However we were not able to demonstrate its existence among the constituents which we could detect in the beam of the dissociation products of the nitrogen molecule.

Keywords : Metastable $^6S_{5/2}$ state of nitrogen, magnetic moments, Stern-Gerlach and time of flight techniques.

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1. Introduction

Being one of the most abundant materials in the nature and essential constituent of life, nitrogen has been the subject of extensive studies since the early days of science. Lavoisier published a list of 33 elements including nitrogen just after the discovery of oxygen by Priestley in 1774. In the following decades the physical and chemical properties of nitrogen have been continuously investigated by scientists.

In 1865, Morren [1] reported the nitrogen afterglow. Since the glowing was found to be chemically active, it was called "active nitrogen". The literature on active nitrogen which has been published after 1945 is reviewed by Wright and Winkler [2] and the work of Mitra [3] provides a survey of the experimental developments prior to 1945. The luminescent and active behaviour of nitrogen may be attributed chiefly to the presence of ground state atoms and excited molecules. However, it is believed that excited nitrogen atoms and nitrogen

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molecules with higher energy content may be responsible for the short-duration afterglows. Among these species, Innes and Oldenberg [4] postulated the existence of the ^6S state in the "auroral" afterglow. This sextet state of the nitrogen atoms was considered metastable with an energy of about 16 ev above the ground state. Although an evidence of possible existence in the laboratory by electron bombardment of nitrogen was reported [5], it has not been detected experimentally until the lifetime measurement of Fairchild *et al* [6]. Using the time-of-flight technique they obtained 100±25 μs for the natural lifetime of these species, and combining their lifetime measurement with the quenching results, they concluded that nitrogen atoms are in the $2s2p^33s$, $^6S_{5/2}$ metastable autoionizing state. The motivation of the studies presented here was to identify these species in the Atomic Beam Machine and to explore the state further by using Stern-Gerlach and magnetic resonance techniques.

Among the dissociation fragments of the nitrogen $^4S_{3/2}$ ground state atomic nitrogen is the most abundant in a beam produced by electron impact or discharge source. The ground electron configuration of atomic nitrogen is $1s^22s^22p^3$. This configuration gives three states, ground state and two low-lying metastable states, $^2D_{5/2,3/2}$ and $^2P_{3/2,1/2}$, respectively, 2.4 and 3.6 ev above the ground state [7]. ^2D has a long lifetime of 26 hours, while the radiative lifetime of ^2P is only 12 seconds. The concentrations of ^2D and ^2P nitrogen atoms, compared to that of ^4S atoms, are expected to be very low among the dissociation products.

2. Experiment

2.1. Apparatus:

The apparatus which has been used throughout these studies was the Berkeley Atomic Beam Apparatus. (Figure 1.) This machine has a length of 2.5 m from the source to the detector.

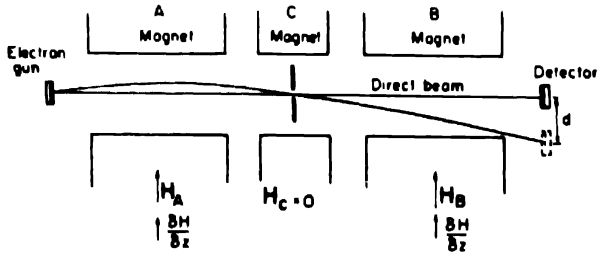

Figure 1. Schematic atomic beam apparatus used as a deflecting time-of-flight analyser.

The field gradient of its in homogeneous magnets is about 100 T/m with a field of 1.0 T. The collimating slit is 0.15–0.25 mm wide and placed in the middle of the C magnet. The source slit-width varied from 0.07 to 0.20 mm and detector slit from 0.30 to 0.60 mm. High-purity grade Helium and Argon gases were used for calibration purposes. Throughout the experiment several types of sources were designed and used. However most of the data were taken by using a particular electron-gun type source. It is shown in Figure 2. Anode voltage

was applied in the pulsed mode, each pulse lasting 13.3 or 40 μs depending whether the faster or slower species were searched. Maximum anode voltage was about 200 V. A regular power supply was switched on and off by a switching circuit which also controlled the

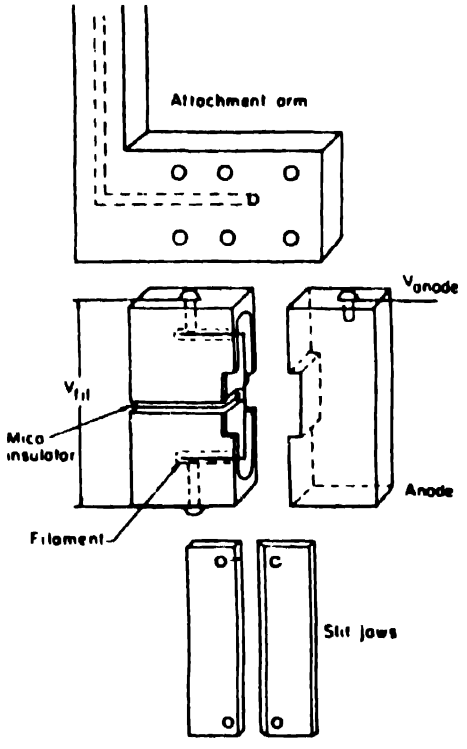

Figure 2. Exploded view of the electron gun. Some mica spacers are not shown for clarity.

operation of data-collecting on-line PDP computer. An illustration of the pulsed mode data collection system is shown in Figure 3. This pulsed-mode data collection technique gives the

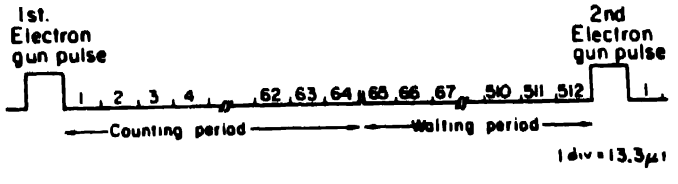

Figure 3. Data collection sequence.

number of particles which are able to reach the detector during their lifetime and sorts them into different channels according to the time they spent in travelling from the source to the detector. Throughout the experiments two scalers were in simultaneous operation. One of them counted the total number of particles in all channels while the other was set to a desired

window of channels, counting only those particles which were in the selected interval of channels.

The detector was a cold tungsten surface followed by a continuous semiconducting film, which served as secondary electron emitter. This magnetic electron multiplier had a gain of 10^7 and was very stable when exposed to the air. It was not sensitive to visible and ultraviolet radiation.

2.2. Method:

Dissociation fragments of nitrogen molecules could be deflected by inhomogeneous magnetic fields. An experiment which combines the Stern-Gerlach and the time-of-flight techniques is expected to give important information on these species.

The deflection of an atom with an effective magnetic moment μ_{eff} and mass M in an inhomogeneous magnetic field is given by

$$d = \frac{1}{2} \frac{\mu_{eff}}{M} \frac{dB}{dz} t^2 \tag{1}$$

where t is the time for the atom to traverse the field and $\frac{dB}{dz}$ is the field gradient. Using a calibration beam of atoms with known μ_{eff} and M_c, one can measure the unknown magnetic moment of any atom.

$$\mu_{eff} = \frac{1}{K_c} M \frac{d}{t^2} \tag{2}$$

where $K_c = (d_c/t_c^2) \cdot (M_c/\mu_{eff.c})$. It is apparent that the constant K_c depends also on the characteristics of the apparatus such as field gradient and geometry. However, a plot of deflection versus t_c^2 which can be written also as

$$K_c = (slope)_c \frac{M_c}{\mu_{eff.c.}} \tag{3}$$

Although the main scope of the experiment was to identify the ^6S state of atomic nitrogen, various parts of the time-of-flight spectrum were also studied. Among those parts are the Rydberg states and the molecular excited states. In a strong magnetic field the effective magnetic dipole moment of the atom is

$$\mu_{eff} = g_j m_j \mu_B \tag{4}$$

where μ_B is the Bohr magneton 9.27×10^{-24} Am^2, m_j is the magnetic quantum number and g_j is the Lande' g factor given by

$$g_j = -1 - \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{5}$$

A schematic Breit-Rabi diagram for N^{14} ($^6S_{5/2}$) is shown in the Figure 4. Expected atomic magnetic dipole moments are written on the right hand side of the diagram.

The experiments we have performed can be treated in three groups:

a) The efforts to obtain a peak in the metastable ^6S region of the time-of-flight spectrum.

b) Several tests on the other species that appear in the fast and molecular regions of the time-of-flights spectrum.

c) The studies to distinguish and prove the identity of those metastable dissociation fragments by deflection and resonance methods.

The first group of experiments were preparatory studies and a peak at about 320 μs was expected to develop. The variables were source pressure, source design, temperature of

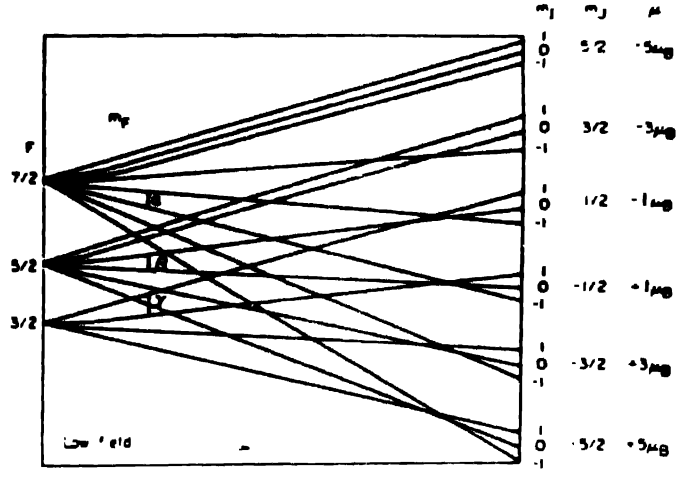

Figure 4. Schematic Breit-Rabi diagram of $^6S_{5/2}$ state of nitrogen atoms with $I = 1$.

the gas, source anode voltage, filament current, electron emission current, slit widths, electron gun pulse-repetition rate. Each run lasted from two minutes to two hours. In most of the runs the magnets were off to avoid deflecting effects. But in some runs the throw-out percentage of various parts of the spectrum, and the quenching effect of the magnetic fields on these species were investigated.

The tests mentioned in part *b* were done to answer the unsolved questions and to gain confidence in the apparatus by detecting well known phenomena of Majarona transitions and measuring the quantities which are already established in the literature. Resonance studies on the $^3S_1$ states of helium [8] and alkali ground states [9], deflection studies on the excited nitrogen molecules, and the studies of the translational kinetic energy of very fast peaks of the nitrogen time-of-flight spectrum versus accelerating voltage of the electron gun can be considered in this group.

The experiments that were expected to be the most fruitful for the purpose fall into the third group. The general procedure was the following : With a certain set of conditions, a time-of-flight spectrum of nitrogen fragments was obtained. This spectrum usually gave a good peak in the expected metastable region when A and B magnets were off and the source, collimator and detector slits were aligned properly. The next step was to bring the detector to one side by a few mils, turn on the magnets and obtain a deflected time-of-flight spectrum.

This routine was followed until the count rate drops down to a very low value as the detector moves with 20 mils steps about 200-300 mils from the centre line. If the species had magnetic moments, inhomogeneous magnetic fields would deflect them to various distances from the centre, depending on their velocity distribution.

In order to determine the effective magnetic-dipole moment μ_{eff} to a reasonable precision, calibration plots which were obtained with the same geometry of the apparatus, the same inhomogeneous magnetic fields and the same time per channel were utilized. The $^3S_1$ and $^3P_2$ metastable states of helium and argon respectively, served very well for this purpose. The results of eight calibration plots with different sets of parameters are listed in Table 1.

Table 1. Calibration chart for determining the atomic magnetic moments.

Slit Widths (mils)	Isotope	I_A (A)	I_B (B)	Time/ch (μs)	μ (μ_β)	K_c
Source 8	He^4	1 8	4.5	13.3	2.0	.206
Collimator 10	He^4	5 0	5.0	13.3	2.0	.300
Detector 25	He^4	1.0	1.0	13.3	2.0	.106
	A^{40}	5 0	5.0	40.0	3.0	2.67
Source 3	He^4	1.8	4.5	13.3	2.0	.208
Collimator 6	A^{40}	1.8	4 5	40.0	3.0	2 04
Detector 12	A^{40}	0.9	1 3	80.0	3 0	3.61
					1.5	3.81
Source 8						
Collimator 12	He^4	1.8	4.5	13.3	2.0	.212
Detector 25						

Certainly, the best and the most precise way to measure the atomic magnetic moments is the atomic beam magnetic resonance method. The Breit-Rabi diagram (Figure 4) of the $^6S_{5/2}$ state of nitrogen atom shows α, β and γ transitions. It was seen that only 1/18 of the $^6S_{5/2}$ atoms were available for a particular transition. Another factor comes from the fact that the flight time of the ^6S nitrogen atoms to the detector is approximately 3 times that of the reported lifetime. In other words only about 5% of the metastable $^6S_{5/2}$ atoms were able to reach the detector without decaying. Therefore the total percentage of the atoms available for transition becomes roughly 0.3% of the $^6S_{5/2}$ atoms which are originally directed toward the detector. In order to increase the transition probability a 3 inches long hairpin was used in connection with a tuning box for good impedence match. Furthermore, this system was controlled for constant oscillation level by a servo system.

2.3. Results and discussion :

After many different arrangements of experimental conditions encouraging time-of-flight spectra were obtained on occasion. A typical distribution is given in Figure 5. The peak

between channels 20 and 35 was expected to represent ^6S metastable state of atomic nitrogen. However, it was not readily reproducible under slightly different conditions. A set of optimum conditions which always produce a peak in this region of channels could not be determined. Besides, the signal to background ratio could not be improved any further.

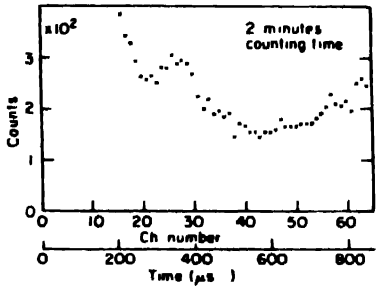

Figure 5. Time-of-flight distribution of dissociation fragments of nitrogen.

The time-of-flight spectrum in Figure 5 has another peak with very high counts between channels 4 and 20. This is called the fast peak in the literature and was speculated [6] as due to neutral atoms or molecules produced by charge exchange of the fast ions in the electron gun. The behaviour of these species was studied by varying the source pressure and electron gun anode voltage. These particles are apparently not ions, since applied magnetic field of 0.5 T would cause them to move in an orbit of a few millimeter radius. The translational kinetic energy of these species was about half or about the same as the electron energy of the electron gun assuming, respectively, neutral nitrogen atoms and molecules. Throw out studies showed that an average of 25% of the particles in this part of the distribution were missing or not reaching the detector while the photon counts were reduced only 8% when the A magnet was turned on to I_A = 5.0 A. The higher anode voltage caused the peak to move toward the faster side of the time-of-flight spectrum. The velocity of the particles in this peak was found to be proportional to the square root of the voltage applied to the anode of the electron gun. Therefore we tend to believe that the fast peaks are due to neutral nitrogen atoms or molecules, most probably high n Rydberg states, emerged from the source at the end of some collisions with electrons, ions, neutral atoms or molecules.

In an effort to gain confidence that the deflection studies yield reasonable results for the magnetic moments, nitrogen molecules in their metastable $A^3\Sigma_u^+$ state were deflected, and, by means of "deflection versus square of time-of-flight" plots, a series of effective magnetic moments were roughly determined. The comparison element was argon with constants K = 3.61 and K = 3.81. The results are in fair agreement with those listed by Freund *et al* [10]. Table 2. makes use of the g_j and J's for N = 0 to 4 taken from the above mentioned calculation and compares the calculated effective magnetic moments with the average value obtained from our two runs. Here N represents the total angular momentum of the molecule exclusive of both electronic and nuclear spin angular momenta. For molecular

structures it is impossible to assign the correct quantum numbers to the effective magnetic moments which are obtained by Stern-Gerlach time-of-flight method. Therefore, our experimental average μ_{eff} values are listed only in decreasing order of magnitude. The first

Table 2. A comparison of the theoretical and experimental magnetic moments (in Bohr Magnetons) from deflection studies on metastable molecular nitrogen.

$\mu_{eff}=^{j}g_{j}$	$\bar{\mu}_{exp}$	$\mu_{eff}=^{j}g_{j}$	$\bar{\mu}_{exp}$
--	4.15	0.67	0.65
--	2.64	0.50	0.54
2.00	1.95	0.40	0.38
1.60	1.67	0.34	--
1.50	1.51	0.30	0.31
1.33	1 35	0.20	0.21
1.20	1.15	0.17	0.16
1.00	1.04	0.10	0 12
0.80	0.86		

two of the values are even not comparable with the values calculated by using their list. Nitrogen $^6S_{5/2}$ metastables having magnetic moments of $5\mu_B$, $3\mu_B$, $1\mu_B$ and a reported lifetime of 100 ± 25 μs should be observed with no difficulty provided that they are produced effectively. Because of the vital importance of production, six different sources and many design and application variations on these sources were tried. About 70 atomic nitrogen deflection runs were performed to search for these magnetic moments. These runs were evaluated by making use of the calibration charts which were also obtained by calibration runs carried out throughout the experiment. A selected sample of the time-of-flight distribution of metastable nitrogen is shown in Figure 6.

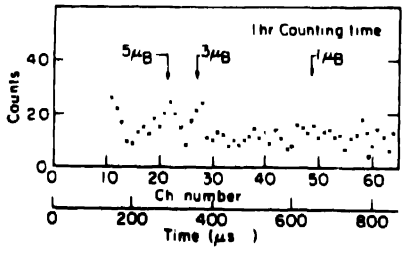

Figure 6. A sample Stern-Gerlach time-of-flight distribution of the dissociation fragments of nitrogen.

This distribution nicely indicates the $5\mu_B$, $3\mu_B$ atomic magnetic moments. The magnet currents were $I_A = 1.8A$, $I_B = 4.5A$. The source slit had a width of 8 mils, collimator slit 10 mils, and detector slit 25 mils. The detector was 30 mils away from the alignment centre. The time for the electron gun pulse and for each channel was 13.3 μs. This data was collected in one hour. As it is seen from the plot the statistics is not very good, and besides, the

distribution could not be repeated under the same conditions. Among the 70 complete runs, each containing about seven distributions only a few time-of-flight distributions gave the expected 5,3 and $1\mu_B$ atomic magnetic moments. It was not possible to follow the displacement of these magnetic moments on the Stern-Gerlach time-of-flight distribution as the detector moved away from the alignment centre. They were intermittently appearing which could also be attributed to the poor statistics. Even when good statistics were acquired, our efforts to differentiate these magnetic moments by the atomic beam magnetic resonance method have failed.

In conclusion, the nitrogen atoms in $^6S_{5/2}$ metastable states are either not produced effectively or have too short lifetime to allow any investigation in our atomic beam machine by the Stern-Gerlach time-of-flight method. This result agrees well with that of the experiments done by Kiefl *et al* [11] who used vacuum-ultraviolet filter technique for identifying the excited dissociation fragments of the Nitrogen molecule.

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